# WASTES IN PRODUCTION

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## MICROSTRUCTURE FORMATION IN CERAMIC MIXES BASED ON TUNGSTEN-MOLYBDENUM ORE FLOTATION-WASTES

**Z. A. Ikramova[1] and M. T. Mukhamedzhanova[1]**

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The results of investigations of the phase compositions and formation of the microstructure of ceramic sintered samples based on the composition kaolin-fireclay-KTMO for the purpose of obtaining ceramic materials with elevated physical chemical properties are presented.

***Key words:*** waste utilization, tungsten-molybdenum ores, ceramic, physical-chemical properties.

Depending on the properties of the clay component solid by-products and wastes from production can perform the following basic functions when introduced into ceramic mixes:

– improve the drying and shrinkage properties;

– intensify sintering processes and the heat resistance of material, and so on [1 – 2].

In the present work, we studied the sintering and formation of the microstructure of ceramic mixes for facing tiles manufactured on the basis of the composition kaolin-fireclay-Kaitash flotation wastes of tungsten-molybdenum ores (KTMO). The chemical properties of the initial materials are presented in Table 1.

Table 2 gives the composition of the experimental mixes which contain 4 – 5%[2] fireclay, 25 – 55% KTMO flotation wastes, and 40 – 70% kaolin clay.

The flotation waste, used in ceramic mixes where it acts as a flux, from the enrichment of Kaitash tungsten-molybdenum ore (KTMO) accelerates sintering and nucleation of crystalline phases [3].

The purpose of the present investigation was to study the phase composition of experimental samples, sintered at different calcination temperatures, by means of x-ray phase, complex-thermographic, petrographic, and electron-microscopic analyses.

The XPA data show that peaks characteristic for the interplanar distances of wollastonite ($d$ = 0.300, 0.320, 0.222, 0.198 nm), quartz ($d$ = 0.425, 0.335, 0.181 nm), and anortite ($d$ = 0.376, 0.322, 0.246 nm), and hematite ($d$ = 0.368, 0.21, and 0.184 nm) are clearly seen in the x-ray diffraction patterns of samples of the mixes 3 with added (46%) KTMO and calcined at 950°C (Fig. 1).

It is known that using raw material with elevated iron oxide content in the production of ceramic articles has large effect on the formation of the glass-phase structure and promotes a decrease of the appearance temperature of the liquid phase by 50 – 70°C [4]. For this reason when the amount of the flotation waste KTMO is increased to 46% even more

[1] Tashkent Scientific-Research Institute of Chemical Technology, Tashkent, Uzbekistan.

[2] Here and below — content by weight.

**TABLE 1.** Chemical Composition of Initial Materials

| Initial materials | Content, wt.% | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $Fe_2O_3$ | $Na_2O$ | $K_2O$ | $SO_3$ | others |
| Angrenskoe enriched kaolin | 62.30 | 23.40 | 1.26 | 0.20 | 1.84 | 0.10 | 0.60 | 0.46 | 9.96 |
| Fireclay | 65.81 | 29.26 | 0.84 | 0.36 | 1.64 | 0.44 | 1.10 | – | – |
| KTMO | 42.15 | 8.62 | 19.00 | 4.50 | 13.45 | 0.44 | 0.21 | 0.02 | 11.23 |

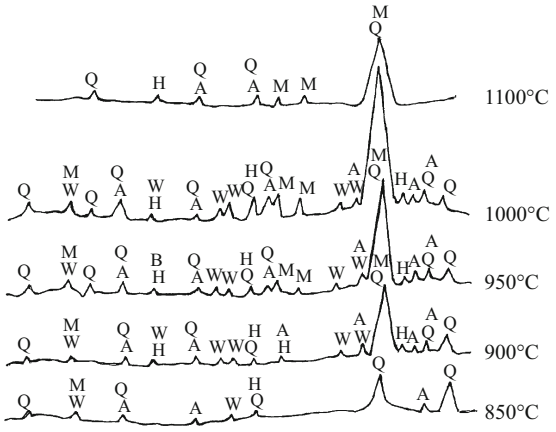


**Fig. 1.** X-ray diffraction patter of samples of the mixes 3 calcined at various temperatures: M) mullite; A) anortite; W) wollastonite; Q) quartz; H) hematite.

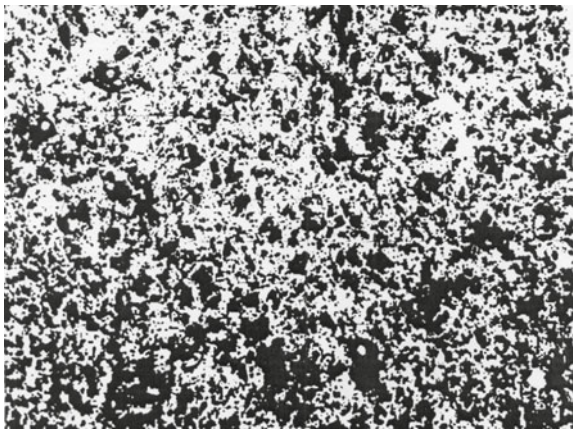

**Fig. 2.** Microstructure of sample No. 3 sintered at 950°C; × 600.

glass is formed. Using an optical microscope, porous glass with different composition was formed. Evidently, the intensification of glass formation when the amount of flotation waste KTMO is increased to 46% is due to an increase of the iron oxide content.

It is evident in the x-ray diffraction pattern (see Fig. 1) of the samples of the mix 3, which were calcined at temperatures above 900°C, that the wollastonite and anortite phases formed at the initial stage of the solid-phase interaction process, are characterized by strongly disordered structure, as is indicated by the weak and diffuse character of the peaks of the primary reaction products. Conversely, the diffraction maxima of wollastonite and anortite seen in the x-ray diffraction patterns of the samples calcined at temperature above 900°C have high intensity. These features of the x-ray diffraction patter, taking account of the morphology of anortite and wollastonite crystals, shows [5] that an ordered crystal structure of calcium silicates is present. The investigation of the phase composition of the mixes calcined at different temperatures (see Fig. 1) indicates that on heating to 800°C new crystalline phases are not formed and quartz remains the main crystalline phase. At this temperature recrystallization of amorphous silica in cristobalite starts. As the calcination temperature increases, the intensity of the cristobalite lines increases while the intensity of the quartz lines decreases.

**TABLE 2.** Charge Composition of the Experimental Ceramic Mixes

| Ceramic mix | Content of the components, wt.% | | |
|---|---|---|---|
| | kaolin | KTMO | fireclay |
| 1 | 70 | 25 | 5 |
| 2 | 60 | 35 | 5 |
| 3 | 50 | 46 | 4 |
| 4 | 45 | 50 | 5 |
| 5 | 40 | 55 | 5 |

The results of the x-ray phase analysis show that anortite $CaO \cdot Al_2O_3 \cdot 2SiO_2$ and wollastonite $CaO \cdot 2SiO_2$ begin to form at calcination temperatures 800 – 900°C; the reaction forming these crystals increases with increasing calcination temperature of the sample. The anortite formation process proceeds at an elevated rate, which is confirmed by the appearance of intense anortite lines in the x-ray diffraction patterns; this is promotes high-temperature shrinkage and densification of the material.

The change of the phase components of ceramic mixes at 950°C improves their physic-mechanical properties (compression strength 50.9 – 65.7 MPa, density 2550 – 2890 kg/m$^3$, water absorption 8.6 – 9.6%) and shrinkage does not increase much (by 1.8%, composition No. 3). Apparently, the formation of wollastonite and anortite curtails the increase of shrinkage [5]. The ultimate bending strength increases by more than 25%.

In connection with the appearance of a liquid phase in the samples at temperature above 1000°C, the intensity of the line of all compounds decreases, indicating that they dissolve in the melt.

Analysis of the complex thermograms of the experimental mixes showed the presence of four thermal effects. An endothermal effect with a maximum in the temperature interval 100 – 110°C, accompanied by a change of the mass of the samples, corresponds to the removal of hygroscopic moisture. With further heating a negligible increase of mass and the appearance of an exothermal effect with a peak at 340 – 400°C, due to oxidation and combustion of organic impurities, are observed. The endothermal effect in interval 540 – 580°C with a peak at 550°C is due to the dehydration of clayey components. The effect is accompanied by substantial mass losses, equal to 5.32%.

The curve of the change in the losses during calcination after the endothermal effect passes evenly into a horizontal position and is virtually unobserved in the subsequent losses.

The exothermal effect in the temperature interval 900 – 950°C with a maximum at 950°C attests to the start of the anortite and wollastonite formation process and the ap-

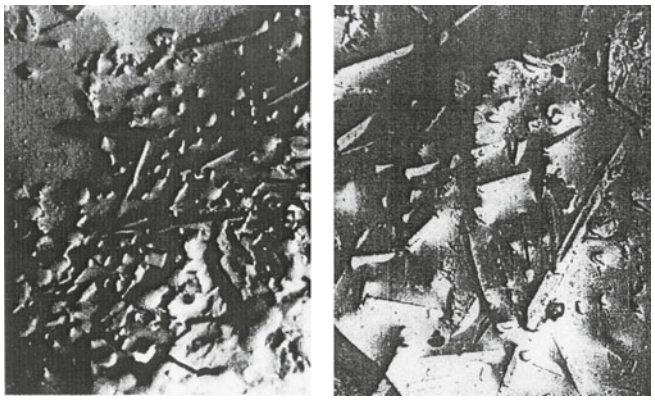

**Fig. 3.** Electron-microscopic photographs of samples with the composition No. 3 sintered at 590°C; × 3000.

pearance of a liquid phase. The densification of the material starts at the peak of the exothermal effect (953°C), which corresponds to mass loss 2.2%.

The process of structure formation in ceramic samples synthesized on the basis of the composition kaolin-firecaly-Kaitash flotation wastes of tungsten-molybdenum ores (KTMO) was studied by petrographic analysis of transparent sections made from the experimental mixes calcined at 950°C and by the electron-microscopy method. Microscopic studies of transparent sections in transmitted light showed that the structure of the sample is nonuniform and that, visually, the sample contains somewhat more quartz and the quartz is slightly fused. The main phase is consists of wollastonite ($N_g$ — 1.631, $N_p$ — 1.616) and anortite ($N_g$ — 1.58, $N_p$ — 1.57), which have an isometric form and are lamellar, colorless, and transparent (Fig. 2).

The electron-microscopic investigation of the structure of the samples with composition No. 3, sintered at 950°C (Fig. 3) showed that the main structural elements belong to prismatic anortite (1.71 – 0.71 nm) and pellet-shaped wollastonite (1.14 – 0.85 nm).

The studies of the structure of the ceramic samples showed that the samples consist mainly of wollastonite, anortite, hematite, and quartz.

In summary, a ceramic material with low sintering temperature was obtained as a result of the studies performed with the composition kaolin – fireclay – KTMO. This will make it possible in the future to expand the raw materials resources for the production of ceramics.

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